Synthesis and characterization of efficient photoelectrodes for photoelectrochemical water splitting

A SYNOPSIS
Submitted for the Award of Degree of
Doctor of Philosophy

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March 23, 2015

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1. Introduction to Solar-Hydrogen

In the fast-paced growth of modern times, one of the most vital competent for sustained development and affluence is the energy; yet many of the countries are striving hard for it to satisfy even their basic requirements. This disparity in the energy availability is partly due to localized distribution of non-renewable sources of energy (viz. coal, petroleum, natural gas and oil) and often the non-optimal utilization of renewable energy (World Energy Outlook, 2011). World's continued heavy dependence on the non-renewable sources of energy, such as fossil fuels, has lead to their rapid depletion, which is being seen as a serious cause of concern. To fulfill the energy needs of mankind and attain the energy security for the upcoming generation, the preference of non-renewable sources of energy should be changed to the renewable and superior forms of energy.

By renewable sources of energy we imply the energy drawn mainly from sun, wind, hydro energy and geothermal energy, all of which account for clean energy reservoirs. Although, we have been deriving energy for many decades from above renewable energy reservoirs in different pockets of the world, but it is only in the last few years that the thrust on renewable energy usage has acquired the pace and significance. Out of the different alternatives available under the category of

renewable energy, solar energy is definitely the most attractive. The earth being the third planet in our solar system (nearly 1.5×10^8 km away from sun) receives roughly 3×10^{24} J/year (Venkata etal., 2011) of solar energy in the form of radiations. It is also a fact that the bulk of this energy from sun to earth actually comes in the form of visible radiations.

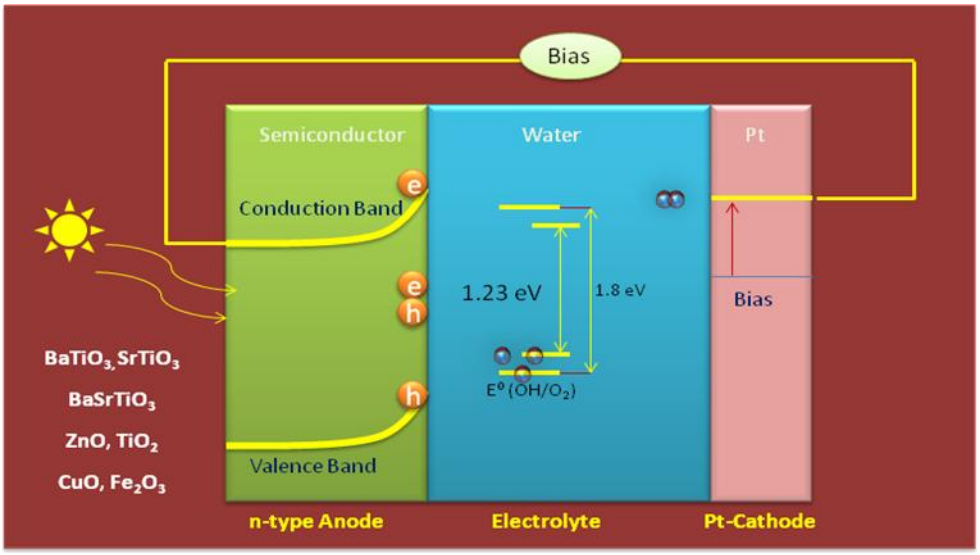
The storage of abundantly available solar energy by its conversion to electricity and/or high energy fuel is possible. The small-scale uses of solar energy, viz. solar cooker, solar heater, other solar powered small gadgets etc. are already in practice. However, the main aim is to develop a technology that would pave the way for large-scale storage and utilization of solar energy in the society. To this extent the researches pertaining to the development and improvement of solar panels (photovoltaic cells) have been great contributor. However, PV cell based solar panels have their own limitations, mainly arising out of their still prohibitive cost and battery requirements. The storage of solar energy to some high energy chemical fuel, viz. Hydrogen, is another option that has drawn the attention of the global community tremendously in recent years. Hydrogen is being seen as a future fuel, a good and clean substitute for fossil fuels, which can be effectively produced from water by inducing splitting of water molecule with the help of solar energy. Photoelectrochemical (PEC) splitting of water is an efficient route to achieve this conversion.

2. Photoeelctrochemical (PEC) water splitting

Exploring the phenomenon of water splitting via PEC route requires an interdisciplinary approach, mandating conceptual understanding of areas like, Chemistry (Electrochemistry, Photochemistry, Interfacial Charge Transfer, and Surface Chemistry), Semiconductor Physics (Electronic Band Structure, Solid State Charge Transport, Optoelectronic Effects) and Material Science. The first scientific study to highlight this concept was probably made by Becquerel in 1839, when they investigated an electrochemical cell, fixed with silver chloride electrode, under sunlight illumination. However, explorations on it attained significance in the year 1972 and thereafter,

when for the first time Fujishima and Honda demonstrated that semiconductor (titanium oxide) under illumination, leads to the oxidation reaction of water at more negative potentials compared to the standard redox potential of the H_2O/O_2 redox couple (Hisatomi etal., 2014). The sustained research of nearly 40 years in this vital area has led to a better understanding on the mechanism of the process and now we are in a much better position to identify the different interlinked controlling parameters to the process.

Working of the PEC cell (exhibiting the water splitting reaction) depends critically upon the properties of the material used as photo-electrode. The two most basic requirements that a material should fulfill are: (a) ability to absorb maximum solar radiation, (b) suitable catalytic properties essential for water decomposition. The photo electrode is equivalent to the heart in the operation of a PEC cell. It should not only be an efficient light absorber but must also be a low-cost material to meet the commercial viability (Bak et al., 2012). Further, with respect to electrochemical and thermodynamical properties, the photoelectrode must also possess following: (a) Band gap between 2-2.2eV, (b) Conduction band at more negative potential than H^+/H_2 redox potential, (c) Valence band at more positive potential than potential of oxygen evolution.



3. Material options and challenges

The success of PEC hydrogen production relies on meeting the significant technical challenges in developing new and effcient materials/material systems (semiconductors) for the process. Representing the most widely investigated class of materials in this context are oxides of metals with d^0 and d^{10} configuration. In the past four decades of sustained research, several metal oxides have been investigated for the PEC water splitting, although none of these materials possess all the properties required (as mentioned above). In general, PEC splitting of water is considered to occur in three steps: (a) photogeneration of charge carrier on the exposure of solar radiation, (b) migration of charge carriers to surface without recombination and (c) reduction and oxidation processes for the production of hydrogen and oxygen via splitting of water. The first and second step depend on the structural and electronic properties of material (s) used, and the last step depends dominantly on the semiconductor-electrolyte junction characteristics. To facilitate the occurrence of step (c), the use of catalysts and co-catalysts has been recommended by few workers. These are known to produce active sites on semiconductor surface and reduce activation energy for gas evolution (Hisatomi et al., 2014). Few previous studies highlight the crucial and wide ranging participation of catalysts/co-catalysts in splitting of water for hydrogen production via preventing the recombination of photo induced charge carriers and speeding up of the gas evolution reaction by lowering the activation energy.

The most widely studied catalysts/co-catalysts are metals (viz. Au, Pt, Rh, Ru, Ir etc) and their oxides. For the splitting of water, the catalyst/co-catalyst should have tendency to inhibit the electron-hole recombination and must favour the oxygen and hydrogen evolution reactions. Among the noble metals, Rh and its oxides are considered to be the efficient catalyst. The scarcity and expensive nature of noble metals prohibits their utilization towards the large-scale hydrogen production (Yang et al., 2012). This has diverted the interest towards transition metals and their

corresponding oxides, hydroxides, sulphides and carbides also, especially the Cu, Ni, Co are proving to be better bet. In recent years, the use of certain non metals, viz. carbon, in form of nanowires, nanotubes (single walled, multilple walled) and graphene has also been advocated. The amount, size and morphology are key factors which seem to govern the role and action of catalysts/co-catalysts in the overall occurrence of the process (Ran et al., 2014).

From the presentation above, it is apparent that there exists an important domain of fundamental research, where working with different semiconductors, variety of catalyst/co-catalysts has been investigated. However, the role and choices of catalysts for water splitting in PEC cell is still a tricky issue that warrants further investigation. Further, in recent years when the thrust is more on combining the advantages of more than one material and to generate a better and more efficient material system for PEC water splitting, the role and significance of catalysts/co-catalysts has assumed tremendous significance. The literature survey reveals that not much work is reported on this aspect, particularly using bi-layered nanostructured thin films of semiconductors.

4. Proposed Study

The proposed plan of work aims to achieve the surface embedding of metal (Ag, Au, Cu) nanoparticles on bi-layered thin film nano-hetero-structures of chosen metal oxides semiconductors, in order to explore the catalytic/sensitization influences of such metal nanoparticles towards the efficient photoelectrochemical splitting of water. The goal here would be to first synthesize bi-layered nano-hetero-structures, where the top layers would be embedded (decorated) with biologically/chemically derived metal nanoparticles. The films, thus obtained, would be subjected to thorough characterization and their use in PEC water splitting would be investigated.

5. Objectives/Stages of the Proposed Work

The main objectives/stages of the proposed work would be as,

1. Synthesis of metal nanoparticles through controlled reduction via biological/chemical routes.
2. The preparation of bi-layered thin film nano-hetero-structures of chosen metal oxides, surface embedded with metal nanoparticles, by wet chemical routes, viz. sol-gel spin coating/spray pyrolysis.
3. The characterization of films for crystallographic, morphological and other semiconductor properties relevant to PEC water splitting.
4. PEC water splitting studies using the films prepared and measurement of the performance indicating parameters.

6. Proposed Methodology

Metal nanoparticles will be prepared from their low-cost compounds via controlled reduction in an aqueous system by chemical/biological routes. In the biological route, appropriate biological (plant derived) materials, viz. spirulina (algae), tea and other plant extracts etc would be employed. Conducting glass plates will be used as substrate for film deposition. Films would be prepared by sol-gel spin coating and spray pyrolysis. Sintering at high temperature would enable the evolution and growth of the desired crystalline phase. In the top few layers of the films, metal nanoparticles would be embedded during the course of films formation. After systematic and thorough characterization of films, these would be subjected to PEC studies.

7. Tentative Plan of the Work

A tentative plan of proposed work has been outlined below in Table 1

Table 1: Tentative plan of the proposed work

Parameters of the study	Description
Preparation of samples • Materials of interest	 ZnO, Cu_2O/CuO, α-Fe_2O_3, Bi_2O_3
• Proposed modifications	▪ Single and bi-layered Nano-hetero-structured thin films (different posible combinations based on the band edge locations/matching) ▪ Single and bi-layered Nano-hetero-structured thin films, surface embeded with metal nanoparticles (viz. Au, Ag, Cu)
• Proposed method for Preparation	*Metal Nanoparticles:* ▪ Biological route ▪ Chemical route *Thin films:* ▪ Wet chemical routes (viz. sol-ge/spray pyrolysis); spin/dip coating
• Variables	▪ Film thickness (to be varied by varying the number of depositions) ▪ Sintering temperature ▪ Surface amount/concentration of embedded metal nanoaparticles
Characterization	▪ Phase analysis by XRD ▪ Surface morphology by SEM ▪ Surface Topography by AFM ▪ Band gap energy by UV-Visible Spectroscopy ▪ Film thickness by surface profilometer ▪ Charge carrier density ▪ Electrical resistivity ▪ Flatband potential
PEC measurement variables	▪ Current-Voltage relationships and IPCE measurements under darkness and illumination. ▪ Photovoltage ▪ Photocurrent ▪ Open circuit potential ▪ Short Circuit current

8. Literature Survey

Presented below is the highlight of few recent works in the proposed area of research.

Lee et al (2011) reported a way of modifying the surface of the metal oxide films via derivative of citric acid bearing an alkyne linkage to enhance the stability of such films. The multidendate carboxlate of the derivative binds itself efficiently to nanoparticles of metal oxide evolved via

Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) reaction. Hence the modular functalization of the films can be performed over the different oxide films.

Shah et al (2012) studied about the modular functionalization of SnO_2, where SnO_2 was synthesized via chemical vapour deposition method. The method yielded nanorod with high –OH density which were converted to azide hence the TiO_2 nanoparticles were covalently bonded to SnO_2 via the Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction. Hence the photovoltage recorded for the corresponding modification yielded a greater enhancement in current density due to decrease in charge recombinations

Yan et al (2013) has worked over the modular functionalization of the metal oxide via click reaction in absence of the catalyst (copper). The metal oxide considered for the study was zinc oxide which was exposed to 1,1-azidodecanoic acid to generate azide linkage binded via –COOH moiety. Further, the functionalization was achieved via reacting it with 1-ethynylpyrene and biomolecule biotin where each functionalization was characterized via different spectroscopic techniques. The only disadvantage prone with this method is the etching of film due to the continuous exposure to different acids.

Upadhaya et al (2013) investigated the co-catalyst, electrocatalyst and photon absorber property of metallic nanoparticles in heterostructures. They followed an approach of fabricating the film *via* modifying the substrates and nano-particles through developing alkyne/azide linkage. The layers of modified nanoparticles were impregnated over the modified substrates leading to enhancing of stability, photolectrochemical and photocatalytic activity.

Bagheri et al (2014) has reported TiO_2 as an alternative support material for heterogeneous catalyst. The need for the support material is reported due to blockage of active site available at catalyst due to agglomeration of particles. They observed that the chemical stability, metal support interaction and certain acid base property have made titanium oxide as efficient support

metal catalyst. The above mentioned properties lead TiO_2 supported metal catalyst to show high photocatalytic activity and application in synthesis of chemicals and as electrodes in solar cells.

Amina et al (2015) studied the effect of promoter over the Ni/Al_2O_3 catalyst prepared via sol-gel method and utilized these for the carbon dioxide reforming of methane. The promoters considered for the above study included elements of lanthanide series as Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm. XRD, TG-DTA, BET surface area, BJH, XPS, Raman, H_2-TPR, and TEM were employed for the characterization of the materials prepared. The result reported states about low conversion yield in promoted catalyst as compared to un-promoted catalyst which was predicted to be due to the smaller pore size in promoted catalyst. In contrast to this, promoted catalysts were found efficient when studies were time based and hence the increasing order of activity for the conversion was termed as un-promoted> Eu > Tb > Ho > Tm > Er > Dy > Pr > Sm > Gd > Nd. Among all lanthanides Er promoted catalysts were efficient in methane conversion.

Qiao et al (2015) has reviewed about different electro-catalyst required for the reduction of carbon dioxide to yield low carbon fuels such as CO, $HCOOH/HCOO^-$, CH_2O, CH_4, $H_2C_2O_4/HC_2O_4$, C_2H_4, CH_3OH, CH_3CH_2OH and others where the literature has clearly reviewed for electro-catalyst to be metals including their alloys, oxides, complexes, enzymes, clusters and organic molecules. They investigated the effects over the properties of catalyst due to variation in electrode potential, solution–electrolyte type and composition, temperature, pressure, which ultimately concluded about the active and stable electro-catalyst required for the reduction of carbon dioxide.

Wang et al (2015) has reported about Pd as catalyst where it is termed as the superior catalyst in terms of oxidation of hydrocarbon and thermal stability of Pt/Rh catalyst. The article reviewed the effect of combination of different catalysts, viz. Pd-only, Pd/Rh, Pt/Rh, and Pt/Pd/Rh along

with different configuration process of close-couple, dual bricks, layered, and zone –coated catalyst.

Park et al (2015) has studied oxidative dehydrogenation of but-1-ene and 1, 3 –butadiene under the influence of catalyst oxide BiV_xMo_{1-x} with varying composition of Bi, V, Mo. They observed that the addition of V in Bi-Mo enhances the catalytic nature, such that the oxide catalyst at stoichiometric ratio of V 0.6 possesses superior oxygen mobility. The catalytic behavior decreased in the order of stoichiometric ratio of V as 0.6 > 0.4 > 0.8 > 0.2 > 0 > 1.

Inkowaa et al (2015) has studied about catalytic behavior of Nickel particles in nano-regime, where the particles were prepared via preventing diffusion and high temperature sintering using the precursor as Ni $(C_5H_5)_2$ over the zeolite. They compared the catalytic properties of nano-particles and the particles derived from conventional methods by studying the kinetic properties and frequency factor and observed high thermal stability and dispersion level prone by Ni nano-particles catalysis.

Gungormez et al (2015) has reported the catalytic behavior of copper-palladium alloy at varying composition in nano-regime to reduce oxide of graphene. The synthesis of mono-disperse nano-particle was carried out by following the micelle method, where acetyl-acetonate complexes of Pd and Cu in surfactant were reduced via morpholine borane complex in solvent oleylamine and 1-octadecene at 353 K. Hence this method yielded Cu/Pd alloy to be formed at varying composition where out of the three composition studied the $Cu_{75}Pd_{25}$ with the size of 3.0 nm showed the higher catalytic efficiency in hydrogen generation from hydrolysis of ammonia borane.

Fakhouria et al (2015) has reported about an enhanced photo-electrochemical and photocatalytic properties for the multi-layered thin film (TiO_2 and TiN) in comparison to un-doped and doped films (N doped in TiO_2). However throughout in their study the number of bi-

layers for multilayered system was kept 9 or 18 whereas the ratio of oxide and nitride of Ti was varied. Hence to yield the best effect of reflection, absorption and charge separation the thickness of the films were controlled to yield ratio in the range of 5 - 28% for TiN and TiO_2 films. They reported maximum current of 21% for the 9 layers and 28% for bi-layer films. The enhanced activity for bi-layer systems as compared to doped and un-doped films of TiO_2 was attributed to efficient charge separation under visible light illumination condition.

Myilsamya et al (2015) synthesized TiO_2 nano-composites doped with varying weights (in percentage) of In and Ce *via* sol-gel route and characterized for evaluation of different physical, morphological, topographical and functional parameters. Hence, doping 0.2% by weight of In and Ce caused the edges of the band to shift in the visible region. Cerium with the +4 oxidation state acts as a good abstracter of electron and bears the tendency to transfer electron to adsorbed molecule for the production of oxygen, which leads to the suppression of charge recombination.

Uparea et al (2015) prepared nickel-promoted Cu-SiO_2 catalyst for the hydrogenation of levulinic acid *via* utilizing formic acid as hydrogen feeder. Hence, the loading of the promoter to catalyst in ratio of 1:3 efficiently yielded 96% of GVL (γ-valerolactone) and 4% of angelica lactone where the above % yield was reported to be varied with variation in molar ratio of promoter and catalyst. The different characterization technique employed also revealed Ni as promoter with well dispersed Cu species being active for hydrogenation and highly stable in its nanoregime.

Liua et al (2015) explored the development of Rh/SiO_2 catalyst for the hydroformylation of ethylene, because of its activity and efficient stability. The catalyst was prepared via tethering diphenyl phosphinopropyl and doping Al as promoter. The catalyst so prepared was characterized by various techniques to reveal its physical and chemical properties. The results

clearly signified the Al which affected the growth and number of Rh atoms. Further, Al promoted the formation of active sites, increased the electron density over P atom and even affected the acidity of the catalyst surface.

Johra et al (2015) has reported different chemical routes for the reduction of graphene oxide. The present study accounted for the production of reduced graphene oxide composite with zinc oxide and titanium oxide *via* hydrothermally reducing graphene oxide in de-ionized aqueous solution of TiO_2 and ZnO at 180 °C. The synthesized reduced graphene composite yielded 63% of photocatalytic activity for 2 hours associated with UV irradiation (100W) while the enhancement in comparison to pure ZnO is due to increased light absorption capacity and reduction in charge re-combination.

Mandala et al (2015) employed soft chemical method for the synthesis of Pd-Cu nano-particles and explored their electrocatalytic activity towards methanol oxidation reaction in medium with pH > 7. The nanoalloy of Pd-Cu ranging between 17-25 nm were prepared *via* templating the corresponding ion with EDTA and finally reducing it by hydrazine. The composition, size and formation of nanoalloy were investigated *via* different characterization technique. The composition Pd-Cu in the ratio of 3:1 showed the efficient catalytic activity to be 659.4 mA mg^{-1} of Pd.

Fernandesa et al (2015) investigated the hydrogen generation in presence and absence of Ru nanoparticles over the irregular and porous carbon films. Ru nanoparticles of size nearly 10 nm were deposited over the high surface area of carbon thin films *via* phase explosion at high laser influence. The hydrogen generation was reported to be six times to the hydrogen production *via* carbon films without Ru particle in ammonia borane hydrolysis. In addition to morphological characteristics, the presence of sp^2 bonded carbon atoms facilitated good scattering of nano-particles and generated maximum number of catalytic active sites. On the other hand, the

catalytic activity was found to decrease with increase in hydrolysis cycle. High hydrogen generation rate of 15.5 L H_2 min^{-1} g^{-1} of Ru and low activation energy of 20 kJ mol^{-1} suggested Ru as efficient catalyst over carbon films.

Kumar et al (2014) reported catalytic steam reforming of ethanol for hydrogen production, as ethanol is expected to yield maximum number of hydrogen per molecule as compared to water, methanol and methane. The catalyst developed by them played a positive role for the hydrogen generation, the effect comparable to the effects of certain noble metals and transition elements, which are reported as the efficient catalyst in literature for hydrogen generation.

Jushoa et al (2015) studied the activity of CuO–ZnO/MSN (MSN: meo-structured silica nanoarticles) catalyst, prepared at varying % weight of Cu and Zn. The characterization of prepared catalyst revealed the variation in number of Si-O-Si bond, oxygen vacancies, Si-O-Zn, and Si-O-Cu. All above manifestations, due to the variation in sequential addition of Cu and Zn over MSN, were important variant affecting the catalytic activity. Further, apart from the catalytic activity, the catalyst played crucial role in de-colorization of dye.

Krysa et al (2015) investigated the photocurrent density for TiO_2 and α-Fe_2O_3 prepared *via* two different methods as: Sol-Gel and High Power Impulse Magnetron Sputtering. The comparative account for two oxides revealed that photocurrent density for TiO_2 under UV illumination is same while in case of α-Fe_2O_3 the photocurrent density is 10 times more in case of plasmatic films as compared to sol-gel derived films. The superiority of films is due to densely packed particles.

Rekhaa et al (2015) studied the hydrogenolysis of glycerol to 1,2 propanediol, at varying ratio of Co to Zn in Co-ZnO catalyst (prepared by co-precipitation method). The catalyst bearing the Co to Zn ratio as 1:1 when employed yielded 70% glycerol conversion with 80% selectivity to

1,2-propanediol. Hence, area of Co metal and concentration of ZnO were observed as the two parameters contributing in hydrogenolysis activity.

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